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Forced-Flow Chromatography of Metal Ions with the Eluent Containing a Color Forming Reagent

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Copper (II), cobalt (II), and zinc (II) are separated with ion exchange chromatography using the eluent containing xylenol orange and ammonium acetate. These eluted ions are detected continuously with spectrophotometric absorption at 580 nm. The separation of zinc (II) and cadmium (II) are also carried out by using the eluent containing xylenol orange, sodium chloride, and hexamine. Copper, cobalt, and zinc ions of 0.2 to 1 μg level can be determined with the peak height calibration curves. A linear relationship between the peak area and the amounts of ions is obtained over the range 0.2 to 4 μg. Cadmium (II) of 0.5 to 5 μg can be determined with the peak height or peak area calibration curves.

INTRODUCTION

Ion exchange chromatography has been commonly used for separation of inorganic ions. Recently, the advances of the resin and the apparatus have drastically reduced the time necessary for separation. For the detection of metal sample in the effluent, spectrophotometry,[1~3] electrochemical method,[4] flame photometry,[5] and radioactivity measurements[6] are available. Each method, however, presents considerable technical difficulties to determine many metals with high sensitivity. In these detectors, the spectrophotometric detection is most popular, and the method usually needs to mix the effluent with a color reagent solution.

This paper describes an attempt for the simple, continuous detection of metal ions in the column effluent by using the eluent containing a high sensitive color reagent, xylenol orange.

EXPERIMENTAL

Apparatus and Reagents

A Yanagimoto liquid chromatograph Model L-1030 was used. The glass column (3 mm i.d. by 300 mm in length) was kept at 60°C with a water jaket. Shodex Ion Exchanger-HP-175 was used as the strongly acidic cation exchange resin. The detector consisted of Hitachi Parkin Elmer 139 spectrophotometer equipped with an 8 μl microflow cell (supplied by Kyowa Seimitsu Co., Ltd.) having a path length of 10 mm.

Copper (II), cobalt (II), and cadmium (II) stock solutions were prepared by dissolving their chloride with 0.1 N hydrochloric acid. A color forming reagent, xy-

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lenol orange (XO) which was purchased from the Dojindo Co. Ltd., Research Laboratories was used without further purification. The eluent was $1.0\text{–}8.0\times10^{-5}$ M XO and 0.5–0.75 M ammonium acetate buffer at pH 5.06–6.03. For the separation of cadmium (II), another eluent which was $1.0\text{–}8.0\times10^{-5}$ M XO, 0.1–1.0 M NaCl, and 0.05–0.5 M hexamethylenetetramine (hexamine) was used.

Procedure

The eluent was previously flowed enough to obtain a constant base line. Metal samples (1–10 μl) were injected into the column with a microsyringe through a septum injector. The absorbance of metal complexes in the column effluents was measured at 580 nm.

RESULTS AND DISCUSSION

Effect of Buffer Concentration on Retention Time

Figure 1 shows the relationship between the ammonium acetate buffer concentration and the retention time of copper (II), cobalt (II), and zinc (II). The retention

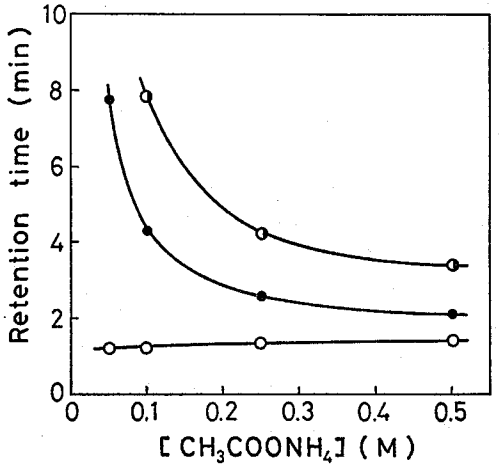

Fig. 1. Effect of CH_3COONH_4 concentration in eluent on retention time.
XO: 4.0×10^{-5} M, pH: 6.03,
Flow rate: 47 ml/h, Temp.: 60°C,
Column length: 20 cm, Metal: 1 μg,
○: Cu, ●: Co, ◑: Zn.

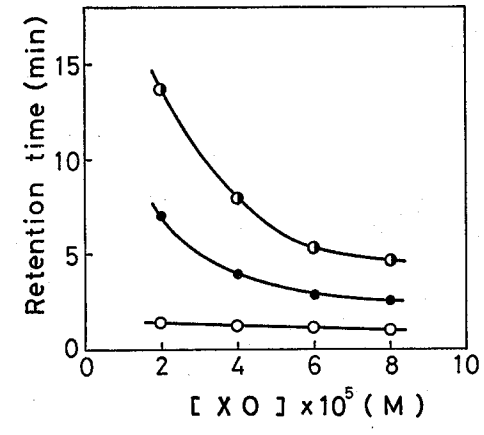

Fig. 2. Effect of XO concentration in eluent on retention time.
CH_3COONH_4: 0.1 M,
Others are the same as in Fig. 1.
○: Cu, ●: Co, ◑: Zn.

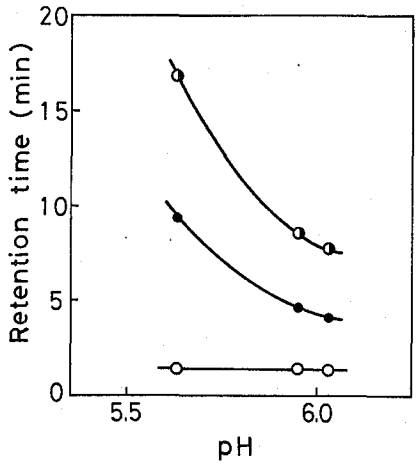

Fig. 3. Effect of eluent pH on retention time.
CH_3COONH_4: 0.1 M,
Others are the same as in Fig. 1.
○: Cu, ●: Co, ◑: Zn.

time of copper (II) is almost constant at various buffer concentrations, but that of cobalt (II) and zinc (II) decreases with an increase of buffer concentration. Although there exists a large difference in the retention time among the metal ions in low ammonium acetate concentration, the difference is not effective for the separation of these metals because of unstable base lines and broaden peaks. Subsequent experiments were carried out at 0.1 M of buffer concentration.

Effect of XO Concentration and Eluent pH on Retention Time

Figures 2 and 3 present the change in the retention time of ions as a function of XO concentration and pH. A decrease of XO concentration or pH leads to insufficiency for coloration. An increase of pH results in an increase in absorbance of XO itself. Then, the eluent containing 4.0×10^{-5} M XO was used at pH 6.03 in the present experiment.

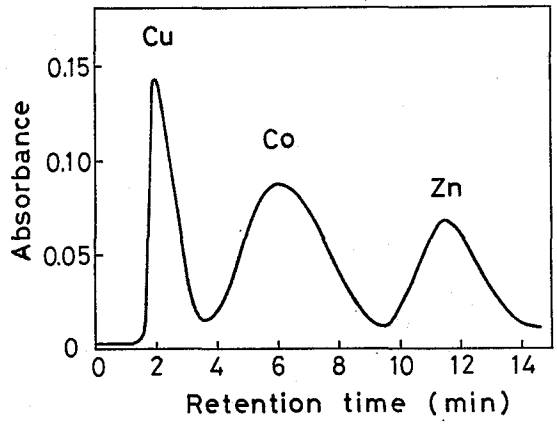

Fig. 4. Separation of copper, cobalt, and zinc.
CH_3COONH_4: 0.1 M, Column length: 30 cm,
Cu, Zn: 0.6 μg, Co: 0.3 μg.
Others are the same as in Fig. 1.

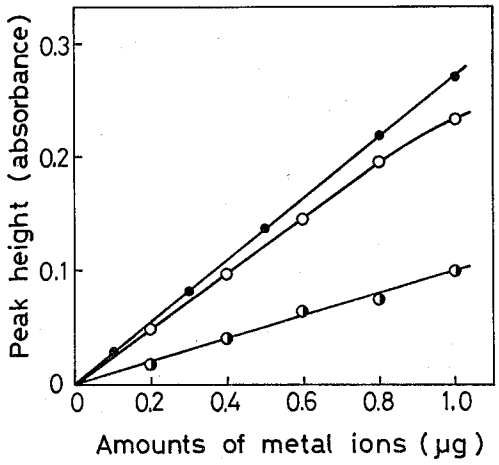

Fig. 5. Calibration curves.
CH_3COONH_4: 0.1 M, Column length: 30 cm,
Others are the same as in Fig. 1.
○: Cu, ●: Co, ◑: Zn.

Separation of Copper, Cobalt, and Zinc

Figure 4 shows a chromatogram of copper (II), cobalt (II), and zinc (II). This separation can be done in less than 14 minutes by using the eluent of 0.1 M ammonium acetate and 4.0×10^{-5} M XO at pH 6.03.

Calibration Curves

Figure 5 shows the relationship between the peak height and the amounts of metals. On any metal ions 0.2 to 1 μg, linear curves are obtained. Figure 6 shows the relationship between the peak area and the amounts of metals. A linear relationship is also obtained over the range 0.2 to 4 μg.

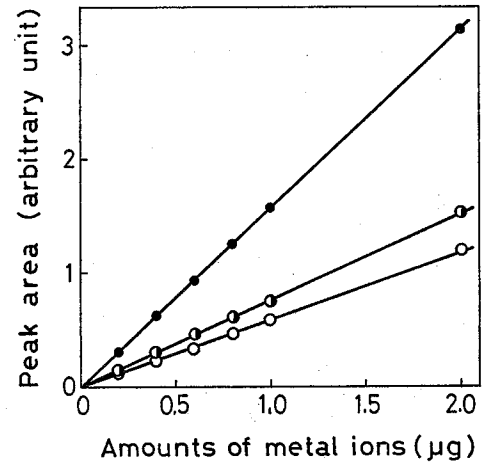

Fig. 6. Calibration curves.
CH_3COONH_4: 0.1 M, Column length: 30 cm,
Others are the same as in Fig. 1.
○: Cu, ●: Co, ◑: Zn.

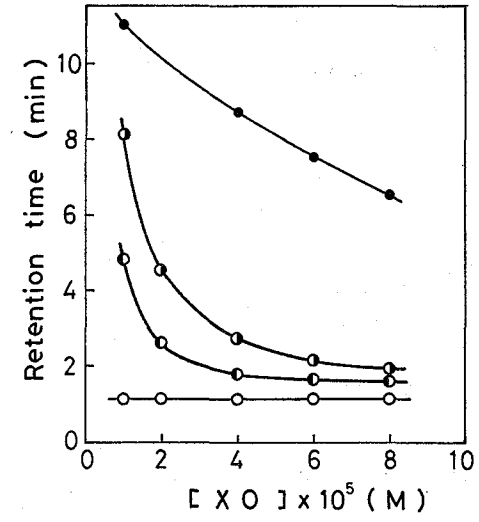

Fig. 7. Effect of XO concentration in eluent on retention time.
Hexamine: 0.1 M, NaCl: 0.5 M, pH: 6.00,
Flow rate: 47 ml/h, Temp. : 60°C,
Column length: 20 cm, Metal: 1 μg,
○: Cu, ◐: Co, ◑: Zn, ●: Cd.

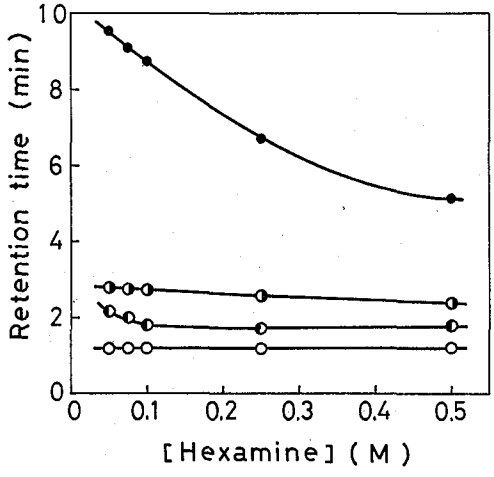

Fig. 8. Effect of hexamine concentration in eluent on retention time.
XO: 4×10^{-5} M,
Others are the same as in Fig. 7.
○: Cu, ◐: Co, ◑: Zn, ●: Cd.

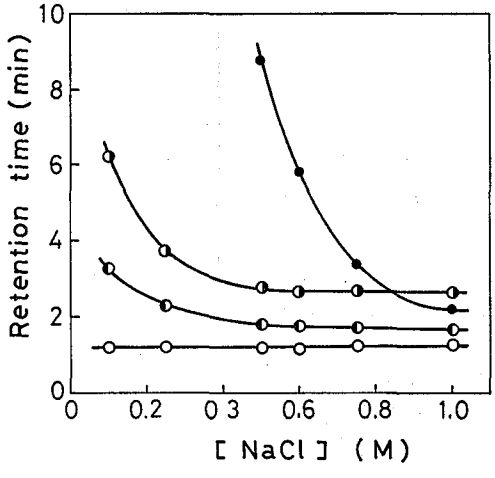

Fig. 9. Effect of sodium chloride concentration in eluent on retention time.
XO: 4×10^{-5} M,
Others are the same as in Fig. 7.
○: Cu, ◐: Co, ◑: Zn, ●: Cd.

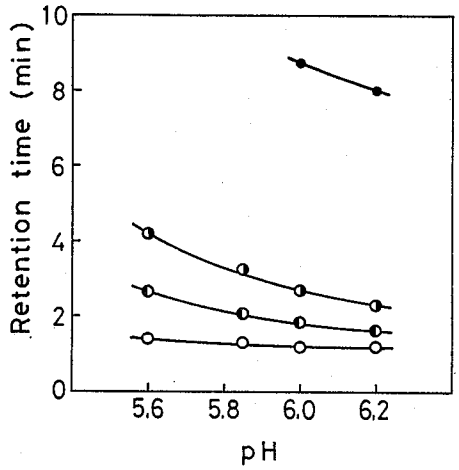

Fig. 10. Effect of eluent pH on retention time.
XO: 4×10^{-5} M,
Others are the same as in Fig. 7.
○: Cu, ◐: Co, ◑: Zn, ●: Cd.

Elution of Cadmium

The color development between cadmium and xylenol orange is disturbed by the acetate ion. For the elution and the detection of cadmium, the eluent containing XO, sodium chloride, and hexamine was used. Figures 7–10 show the effect of XO, hexamine, NaCl, and pH on retention time, respectively. Sodium chloride concentration seriously affects the retention time of cadmium. Figure 11 shows the separation chromatogram of zinc and cadmium. The retention time of copper and cobalt is similar to that of zinc. Therefore, cadmium can be also separated from copper or cobalt. Figures 12 and 13 show calibration curves. Cadmium (II) of 0.5 to 5 μg can

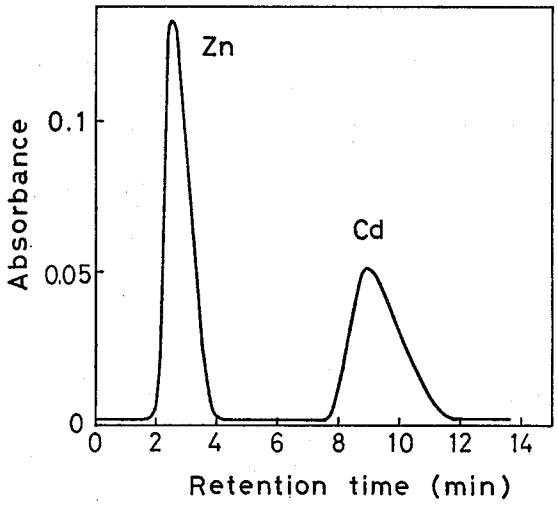

Fig. 11. Separation of zinc and cadmium.
XO: 4×10^{-5} M, Zn: 0.6 μg, Cd: 2 μg.
Others are the same as in Fig. 7.

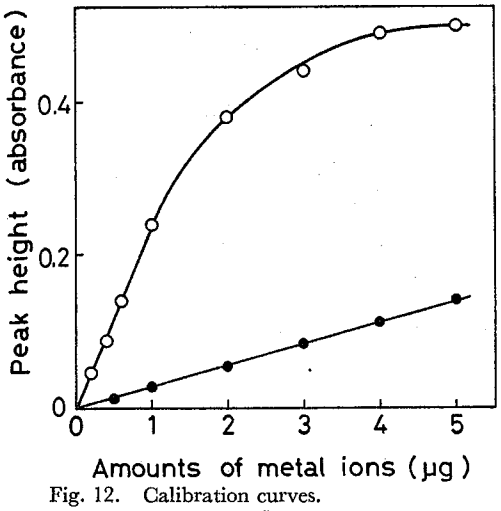

Fig. 12. Calibration curves.
XO: 4×10^{-5} M,
Others are the same as in Fig. 7.
○: Zn, ●: Cd.

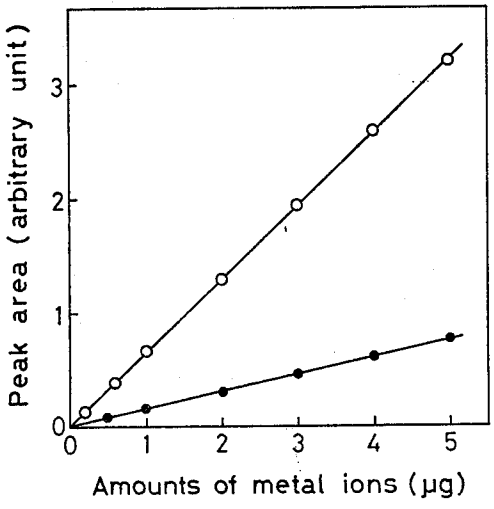

Fig. 13. Calibration curves.
XO: 4×10^{-5} M,
Others are the same as in Fig. 7.
○: Zn, ●: Cd.

be determined with the peak height or peak area calibration curves.

Described above, the use of the eluent containing XO was able to simply analyze small amounts of copper, cobalt, zinc, and cadmium in a short time.

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